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Abstract

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A. I. LEVIN and S. S. SAVEL' EV

ON THE MECHANISM OF ANODIC FORMATION OF DICHROMIC ACID

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The direct electrochemical method for obtaining dichromic acid is based on the use of the equilibrium established between chromate anions in the absence of current (^{1}):

$$2CrO_4^{2-} + 2H^+ leftarrows 2HCrO_4^- leftarrows Cr_2O_7^{2-} + H_2O.$$

As experiment shows (^{2}), with decreasing pH and concentration of an electrolyte containing chromic anhydride, the indicated equilibrium shifts to the right, i.e., toward the formation of $Cr_2O_7^{2-}$.

It may be expected that the desired changes in the ionic equilibrium are subject to definite kinetic regularities. Indeed, from consideration of the electrode processes in a chromate bath (^{3}) it follows that, at a sufficiently high potential created at the anode during electrolysis, a very sharp shift of the pH of the anolyte into the acid region is observed. If an aqueous solution of sodium dichromate is taken, then at high current density, owing to considerable polarization, the predominant anodic process may be the reaction of formation of isopolychromic acids of the type: $H_2O\,(Cr_2O_3)_n$, i.e. $H_2Cr_2O_7$, $H_2Cr_3O_{10}$, $H_2Cr_4O_{13}$, with the formation of chromic anhydride, which is concentrated in the near-anode layers in the form of dichromic acid and its analogues.

For the practical realization of the reaction, anodic processes were considered in a bath having some similarity to mercury electrolyzers used in the production of chlorine and alkali:

$$Hg^- \mid H_2O,\ NaOH \parallel H_2O,\ Na_2Cr_2O_7,\ H_2Cr_2O_7 \mid PbO_2^+.$$

The anodic and cathodic spaces are separated by a diaphragm, and lead dioxide serves as the anode. During electrolysis, alkali is formed in the catholyte, and in the anolyte a polychromate solution is formed, containing, in addition to sodium dichromate, dichromic acid, the concentration of which increases as electrolysis proceeds.

Consideration of the possible anodic processes on a lead dioxide electrode shows that discharge of hydroxyl ions here is accompanied by high polarization (^{4}). At sufficiently high current density at the anode, the final result is an increase in the concentration of $Cr_2O_7^{2-}$ ions and an increase in the acidity of the electrolyte. In this case the activity of OH^- ions is considerably lowered, and the potential of their discharge becomes very high.

Precisely because the anodic oxidation of hydroxyl ions in strongly acidic solutions is accompanied by noticeable retardation, it becomes poss—

possible course of other processes. It may be assumed that one of the following processes will occur at the anode:

$$2H_2O - 4e \to O_2 + 4H^+ \qquad \varphi_1 = \varphi_1^0 + \frac{0.0002\,T}{Z} \lg \frac{[H^+]^4[O_2]}{[H_2O]^2}; \tag{1}$$

$$2H_2O - 2e \to H_2O_2 + 2H^+ \qquad \varphi_2 = \varphi_2^0 + \frac{0.0002\,T}{Z} \lg \frac{[H^+]^2[H_2O_2]}{[H_2O]^2}; \tag{2}$$

$$H_2O - 2e \to O + 2H^+ \qquad \varphi_3 = \varphi_3^0 + \frac{0.0002\,T}{Z} \lg \frac{[H^+]^2[O]}{[H_2O]}, \tag{3}$$

of which it is known[5] that φ_1, φ_2, and φ_3, calculated from the free-energy values of reactions (1), (2), and (3), are respectively equal to 1.229, 1.776, and 2.42 V. The high value of the equilibrium potential of reaction (3) shows that the formation of atomic oxygen according to equation (3) in the presence of $Cr_2O_7^{2-}$ ions is possible only if the oxidation of bichromate anions occurs with a large overvoltage. However, as follows from Fig. 1, the value of the anodic potential φ_a in a bath containing sodium bichromate, even at a considerable current density, does not reach the value φ_3.

It may apparently be concluded that the oxidation of water at the anode proceeds with the formation of molecular oxygen (reaction (1)), and not atomic oxygen (reaction (3)).

According to Glasstone[6], all irreversible processes of anodic oxidation proceed through the intermediate formation of hydrogen peroxide, i.e., according to scheme (3). If this hypothesis is followed, it may be assumed that the process of obtaining bichromic acid must also proceed through the stage of primary formation of H_2O_2 at the anode. Nevertheless, such a discharge mechanism under the conditions considered is unlikely. Because of the very considerable concentration of bichromate anions and the low activity of H_2O in the near-anode layers, the rate of formation of H_2O_2 must be very small. As a result, the potential φ_3 of the reaction of hydrogen peroxide formation is shifted in

Fig. 2. Dependence of the current efficiency of $H_2Cr_2O_7$ on the initial concentration of $Na_2Cr_2O_7$, *a*—saturation at 30°; *b*—at 35°; *v*—at 40°; *g*—at 45°

Figure 1: Fig. 2. Dependence of the current efficiency of $H_2Cr_2O_7$ on the initial concentration of $Na_2Cr_2O_7$, *a*—saturation at 30°; *b*—at 35°; *v*—at 40°; *g*—at 45°

the positive direction. If it is further taken into account that, in the absence of a depolarizer, hydrogen peroxide rapidly decomposes (into water and oxygen), then it may be concluded that the negligible amounts of H_2O_2 formed here will not have time to exert any appreciable oxidizing action. Thus, the influence of hydrogen peroxide on the kinetics of formation of bichromic acid may be neglected.

Fig. 1. Change in the anode potential φ_a with increasing current density i_a in a solution of $Na_2Cr_2O_7$, 1 –500 g/l; 2 –700 g/l.

At the same time, the decrease in water in the anolyte observed during electrolysis of sodium bichromate solutions indicates that a process of its decomposition is occurring. This apparently takes place according to reaction (1), which, however, also proceeds at a lower rate the higher the content of sodium bichromate in the initial solution. The noted circumstance makes it possible to conclude that the optimal conditions for electrolysis of sodium bichromate lie in the region of high concentrations of $Na_2Cr_2O_7$ in the electrolyte. In this case, the prevailing anodic process is the reaction of formation of free bichromic acid and its analogs—isopolyacids—through the direct participation of $Cr_2O_7^{2-}$ anions in the anodic process.

From consideration of the anodic process it is not difficult to see that the high activity of the ions $Cr_2O_7^{2-}$ in the anolyte favors the reaction producing dichromic acid and retards all the other processes. In favor of the point of view expressed is also the circumstance that the current efficiency of chromic anhydride (Fig. 2) rapidly increases with increasing concentration of sodium dichromate; in this case compounds $Na_2O(CrO_3)_n$ are formed.

Almost the only electrode material suitable for carrying out the process of formation of free acid is lead, on whose surface dioxide is formed at a higher rate than the discharge of OH^- or H_2O at their given concentrations. In the case of discharge of $Cr_2O_7^{2-}$ anions, lead acts as a catalyst, which is connected with the formation on its surface of lead dioxide, playing the role of a special oxygen carrier ([7]). The electrochemical process of formation of dichromic acid cannot be carried out successfully if its rate is low. Therefore it is necessary to ensure that the volume of electrolyte, which determines the concentration of the solution, and the amperage load on the bath are in a strictly definite ratio.

Fig. 2. Dependence of the current efficiency of $H_2Cr_2O_7$ on the initial concentration of $Na_2Cr_2O_7$, *a*—saturation at 30°; *b*—at 35°; *v*—at 40°; *g*—at 45°

During the short period of time in which a large amount of dichromic acid is formed, its hydrolysis does not have time to occur. Therefore, at a high volumetric current density and rapid removal of the acid formed in the anolyte, the current efficiency increases noticeably. Side reactions that reduce the current efficiency of dichromic acid during electrolysis are best eliminated if the amount of anolyte in the space between the diaphragm and the lead anode is extremely small. The anolyte must be in the form of the thinnest, continuously circulating layer. Circulation is also necessary so that the dichromic acid, formed in large quantity, is immediately removed from the anolyte.

The direct electrolytic production of dichromic acid, and of polychromic acids contained in polychromate solutions, is of practical interest, since from such electrolytes it is subsequently possible to obtain cathodic deposits of compact chromium.

Ural Polytechnic Institute
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Note: Figure translations are in progress. See original paper for figures.